4-Methoxyhomophthalic acid[1a] (I) on condensation with acetic anhydride in presence of pyridine or fused sodium acetate on boiling water-bath for two hours, furnished 4-carboxy-7-methoxy-3-methylisocoumarin (II) [Needles from ethyl acetate, m.p. 210–211°. Found: C, 61·3, H, 4·7; $C_{12}H_{10}O_5$ requires, C, 61·5; H; 4·3]. It gave U.V. absorption characteristic of the isocoumarins,[1b] $\lambda^{max.}_{(MeOH)}$: 230, 270, 348 mμ; log ϵ, 4·46, 4·06, 3·71. The isocoumarin (II) on refluxing with aq. NaOH for one and half hours and then acidifying with HCl furnished 2-carboxy-4-methoxybenzyl methyl ketone (III) [Needles from water, m.p. 133–34°, Found: C, 63·2, H, 5·9; $C_{11}H_{12}O_4$ requires C, 63·4, H, 5·7]. The ketone (III) cyclodehydrated on keeping with sulphuric acid overnight at room temperature to give 7-methoxy-3-methylisocoumarin (IV) [Needles from petrol ether (60–80°), m.p. 93–94°. Found: C, 69·5, H, 5·6; $C_{11}H_{10}O_3$ requires, C, 69·4, H, 5·2]. U.V. absorption, $\lambda^{max.}_{(MeOH)}$ 230, 269, 348 mμ; log ϵ, 4·53, 4·03, 3·60.

Condensation of 4-methoxyhomophthalic acid with propionic anhydride in the presence of pyridine takes place in similar way to give 7-methoxy-3-ethylisocoumarin by the same sequence of the reactions [Needles from petrol ether (40–60°), m.p. 45–46°. Found: C, 70·4, H, 5·8; $C_{12}H_{12}O_3$ requires, C, 70·5, H, 5·8]. It shows U.V. absorption in MeOH with $\lambda_{max.}$ 229, 269, 348 mμ; log ϵ, 4·54, 4·04, 3·62.

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Organic Chemistry Research Laboratory, Institute of Science, Bombay-1, *December* 18, 1967,

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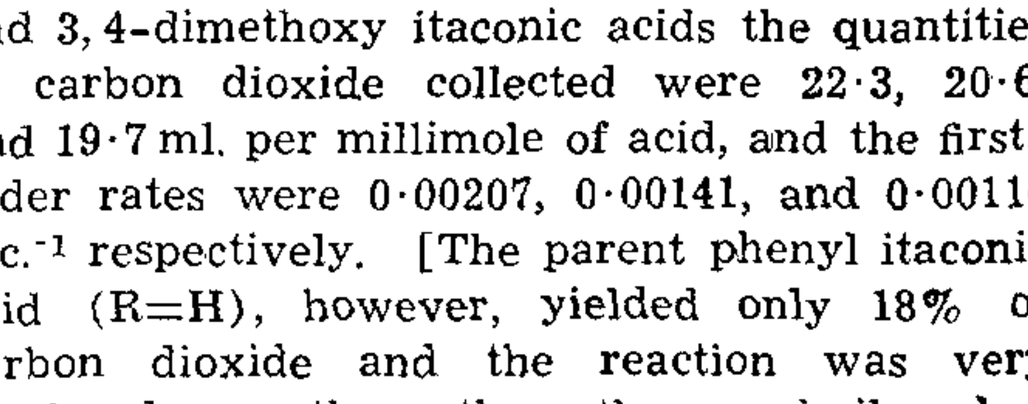
ACID CATALYSED DECARBOXYLATION OF ITACONIC ACIDS

The S_E2 mechanism of decarboxylation of organic acids, where a proton displaces a carboxyl group, was suggested by Schenkel and Schenkel-Rudin[1] on basis of their work on anthracene-9-carboxylic acid. Later, Johnson and Heinz[2] showed that the electronic effects of substituents in the decarboxylation of substituted cinnamic acids were in accordance with this mechanism.

If the mechanism were of the S^a2 type, then the presence of electron releasing groups should facilitate it, since the reaction proceeds through a carbonium ion intermediate[2]; hence acid decarboxylations of some itaconic acids were studied. Decarboxylations were conducted in a manner similar to that adopted by Johnson and Heinz,[2] using a large excess of refluxing $CH_3COOH : HBr(48\%) : H_2O :: 3:2:1$ mixture.

In the case of substituted phenyl itaconic acids the reaction proceeded smoothly with evolution of nearly molal quantities of carbon dioxide, and the decarboxylation showed excellent first-order kinetics. Under identical conditions, for 4-methoxy, 3,4-methylenedioxy, and 3,4-dimethoxy itaconic acids the quantities of carbon dioxide collected were 22·3, 20·6, and 19·7 ml. per millimole of acid, and the first-order rates were 0·00207, 0·00141, and 0·00114 sec.$^{-1}$ respectively. [The parent phenyl itaconic acid (R=H), however, yielded only 18% of carbon dioxide and the reaction was very much slower than the others; similar behaviour for cinnamic acids have been noted.[2]]

The agreement of these reaction rates with Hammett's σ constants, $-0·268$, $-0·159$, $-0·117$ for the corresponding groups[3] gives a quantitative support to a carbonium ion transition state,[2] and the mechanism may be schematically written as below. Further, it reveals that it is reasonable to extend qualitatively (at least) the Hammett's constants to phenyl conjugated systems as in this case.



The itaconic acids used were prepared by the Stobbe condensation of the aldehyde and

dimethyl succinate using methanolic sodium methoxide.[4]

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A COMPARATIVE STUDY OF THE NITROGENOUS CONSTITUENTS OF SOME LEGUMINOUS SEEDS

ALTHOUGH all leguminous seeds hitherto examined—edible as well as wild and uncultivated—have appreciable high protein content, their inclusion in animal nutrition has scrupulously been avoided. This is partly due to their unpleasant odour and taste but mainly due to the deleterious physiological effects which they can exert in the presence of anti-growth and other toxic factors if and when present. This investigation was undertaken with a view to explore the possibility of isolating the different protein fractions from such undesirable wild seed constituents in the pure form and to incorporate them in animal nutrition.

The following describes the distribution of nitrogen in the seeds of *Dolichos biflorus*, *Glycine hispida* (edible but not very popular), *Mucuna pruriens* and *Pithecellobium dulce* Benth. (wild and inedible) as well as the extraction, precipitation, fractionation and partial purification of their various protein components by simple methods.

Healthy and dry mature seeds of *Dolichos biflorus* and *Glycine hispida* were bought in Ranikhet, and *Mucuna pruriens* and *Pithecellobium dulce* seeds were bought locally. The seeds were powdered to 100 mesh, defatted with petroleum ether (B.P. 40–60°) and employed for all investigations.

The preliminary analyses, summarized in Table I, were carried out by methods referred in our previous communications.[1-4]

The effect of pH variation (0·2–10) on the extraction of seed-proteins was studied by employing solutions of HCl and NaOH of known concentration and pH. Weighed samples (*ca* 1 g.) in duplicate were mechanically shaken with the extractants (25 ml.) in Erlenmeyer flasks for 2 hours at room temperature (30° ± 1°). The extracts were centrifuged and nitrogen was determined in 5 ml. of the clear supernatant.

TABLE I
Chemical composition of some leguminous seeds

Constituents		*Dolichos biflorus*	*Glycine hispida*	*Pithecellobium dulce*	*Mucuna pruriens*
Moisture	% ..	3·00	2·73	2·36	4·50
Ash	% ..	3·06	5·22	3·00	4·19
Lipids	% ..	2·02	9·64	11·69	8·64
Crude protein (N × 6·25)		27·62	52·80	24·40	27·56
Total soluble carbohydrate	%	6·93	16·48	19·01	..

Figure 1 representing the variation of extraction of nitrogenous components of seed meals

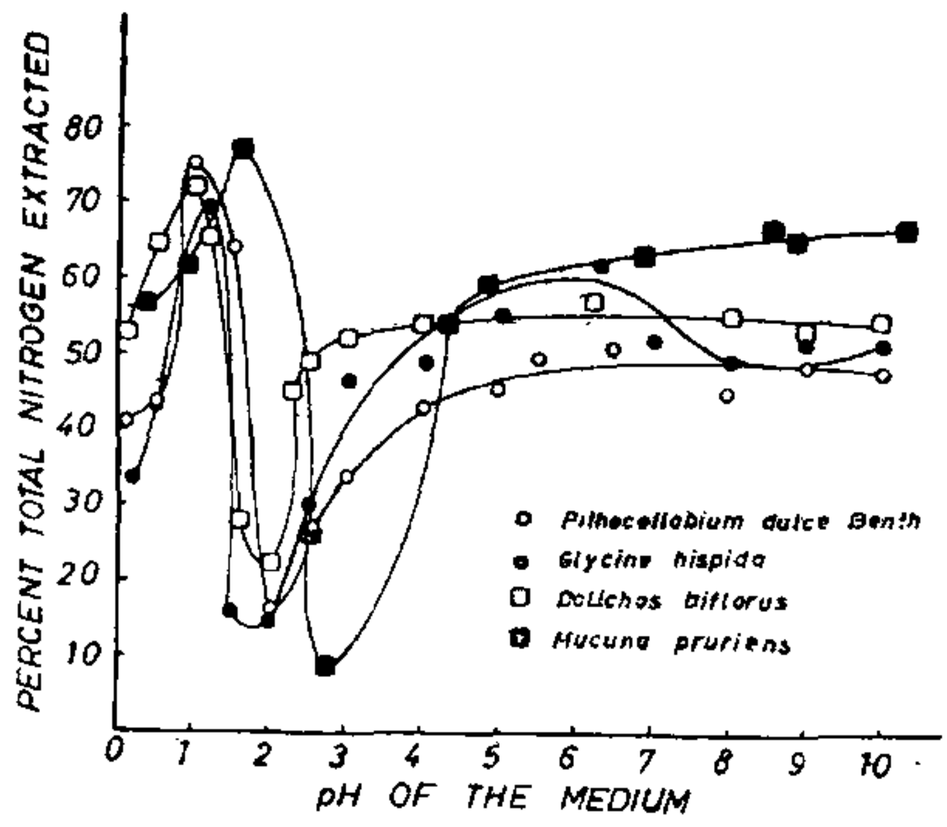

FIG. 1

with the change of pH suggests a method for their isolation. The nitrogenous compounds which mainly consist of proteins and some non-protein nitrogenous compounds (5–6%, Table II) can be maximally extracted with either HCl or NaOH solutions at appropriate pH and then precipitated by adjusting the pH of the medium to that of minimum extraction. However it has been observed by us that these maximally extracted proteins do not get completely precipitated after pH adjustment due to the formation of NaCl which brings about the dissolution of globulins. Therefore, the simplest method for the isolation of seed proteins would be their extraction with NaCl solution at neutral pH and subsequent dialysis of the extract when globulin type of proteins would get precipitated leaving the other soluble ones in solution which could be recovered by suitable precipitants. The proteins thus isolated